THE SEASONAL DEPENDENCE OF ATMOSPHERIC DEPOSITION AND CHEMICAL TRANSFORMATION RATES FOR SULFUR AND NITROGEN COMPOUNDS

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1. Introduction

The objective of this report is to compare wintertime deposition and chemical transformation rates for sulfur and nitrogen compounds with the corresponding summertime values, in order to determine if, on the basis of current theoretical and experimentally determined information, there are significant differences between the summer and wintertime parameters commonly used in mathematical long-range transport models - differences which should be taken into account by the modellers. The objective was not to recommend values of deposition/transformation rate parameters to be used in current models: indeed, in some of the relevant areas (e.g. dry deposition of particulate sulfur and nitrogen, or in-cloud processes) our lack of understanding seems to preculde any such recommendations at present. Due to time limitations, an exhaustive and critical review of the literature was not possible. However, it is hoped that the most relevant scientific investigations have been included in this report.

Chapter 2 deals with wet and dry deposition of sulfur dioxide and sulfates, both from the viewpoint of general theoretical considerations and the results of relevant field and laboratory studies. Chapter 3 takes the same approach with regard to chemical transformation rates. Since information on nitrates is so scarce, all the relevant data on these compounds are summarized in Chapter 4.

The conclusions of this investigation are presented in Chapter 5, where some recommendations are made for modellers concerning the seasonal dependence of deposition/transformation rates, and areas badly needing further study are identified.

2. Atmospheric Deposition

2.1 Wet Deposition

The atmospheric wet deposition of particulate matter and gases has usually been parametrized either in terms of a scavenging coefficient Λ or a washout ratio W (e.g. Dana, 1979). The former results from the assumption that wet deposition is an exponential decay process (since particles or gases are repeatedly exposed to cloud or precipitation elements, with some chance of collection for each exposure) obeying the equation:

$$C_t = C_o \exp(-\Lambda t) \qquad (1)$$

where

C_t = atmospheric concentration at time t
C_o = atmospheric concentration at time zero,
Λ = scavenging coefficient (in units of time $^{-1}$).

The washout ratio is defined as the concentration of contaminant in precipitation divided by its concentration in air (usually at the surface level), i.e.,

$$W = \frac{X}{C} \qquad (2)$$

where

X = concentration of contaminant in precipitation
C = concentration of contaminant in unscavenged air
W = washout ratio (dimensionless).

Most of the discussion to follow will be in terms of the scavenging coefficient, but the same considerations apply to the washout ratio, since Λ and W can be related. For example, for the simple case of pollutant washout from a column of air having a uniform concentration over height h, one obtains:

$$\Lambda = \frac{WJ}{h} \qquad (3)$$

where

J = the precipitation intensity.

2.1.1 General Considerations

When comparing wet deposition rates by rain and snow, it is convenient to express the scavenging coefficient as follows (Engelmann, 1968; Slinn, 1977):

$$\Lambda = \int_0^\infty FEA\,dD \qquad (4)$$

where

A = the cross-sectional area of drops of diameter D
F = the flux density of drops with diameter between D and D+dD (drops/area - time - diameter interval)
E = the collection efficiency (i.e. the fraction of particles or gas molecules in the path of the drop which are washed out by it). For particulates the collection efficiency depends not only on the size of the droplet/snowflake, but also on that of the particle under consideration.

The following approximations to Equation (4) have been suggested for rain and snow scavenging (Slinn, 1981):

For rain,

$$\Lambda \approx \alpha \frac{JE(D_m)}{D_m} \qquad (5)$$

where

α = a constant

D_m = mean raindrop size

$E(D_m)$=collection efficiency of drops with diameter D_m

For snow,

$$\Lambda \approx \beta \frac{JE(\lambda)}{D_s} \qquad (6)$$

where

β = a constant

λ, D_s = characteristic snowflake dimensions which depend on crystal type (see Slinn, 1981)

$E(\lambda)$=collection efficiency of snowflakes having characteristic dimension λ.

A consideration of Equations (5) and (6) suggests a number of factors which could lead to differences between summer- and winter-time scavenging coefficients.

(i) The scavenging coefficient depends on the precipitation intensity, which can have seasonal variations at any given location.

(ii) It is also a function of the raindrop/snowflake size distribution and effective scavenging area. In this connection it should especially be noted that compared to rain, snow has a large surface area-to-mass ratio, and thus is potentially a much more effective scavenger of aerosol particles than is rain (Knutson and Stockham, 1977). However, there is also a strong dependence on the type of snow. Plane dendrites, for example, are predicted to be much more effective as scavengers than graupel (Slinn, 1977).

(iii) For aerosol scavenging, the value of E depends on the size and chemical composition of the particles, because several processes which depend upon these factors are involved during within- and beneath-cloud scavenging (rainout and washout respectively), including Brownian motion, phoretic attachment, inertial impaction and nucleation (see, for example, Slinn, 1977; Scott, 1978). Actually, for an atmospheric aerosol consisting of a mixture of different sizes, the right-hand side of Equations (4) to (6) should be integrated over all aerosol sizes, and even relatively simple theoretical considerations indicate a resulting strong dependence of Λ on aerosol size distribution (Hales, 1978). Hence, the scavenging coefficient for particles could have a strong seasonal variation if the particle size distribution and chemical properties vary due to seasonal changes in emission characteristics, meteorological factors such as temperature and relative humidity, or atmospheric chemical reaction mechanisms, for example.

(iv) The collection efficiency of gases in Equation (4) depends on the solubility and chemical reactivity of the gas in water, and a number of other factors related to interfacial transfer between raindrop/snowflake and the ambient air- see, for example, Hales (1978) and Barrie (1978) for more detailed discussions for the case of sulfur dioxide scavenging. With reference to seasonal variations in the gas scavenging rate, snow scavenging is usually negligible compared to rain scavenging because of low gas adsorption rates on ice crystals (Engelmann, 1968; Slinn, 1981). However, the type of snow should again be considered, since wet snow can have a much higher gas scavenging efficiency than dry snow (Summers, 1977; Hales et al., 1971). Also, it should be noted that for sulfur dioxide, due to the nature of its solubility characteristics in water, the scavenging coefficient is expected to depend strongly on seasonal variations in the ambient temperature and precipitation pH (Barrie, 1981).

(v) There is one more factor, which is implicit in the above discussion, but perhaps deserves elaboration - viz., the importance of seasonal variations in storm type at a given geographical location. This is especially important with regard to in-cloud (rainout) processes, because the mechanisms whereby particles and gases are removed by such processes can depend strongly on the storm type. For example, Scott (1978) has discussed the dependence of sulfate rainout upon the mechanism of precipitation formation (-it should be noted that rainout is thought to be the dominant process responsible for particulate sulfur removal on a regional scale - see, for example, Scott (1978) and Garland (1978)), and has predicted scavenging rates to differ by a factor of 10 or more depending upon whether or not the precipitation originated as snow. Similarly, Summers (1977) has shown striking differences in removal rates of sulfur dioxide by summertime convective storms and snowstorms. These results will be discussed in more detail in the following section.

2.1.2 Experimental Results

For comparing wet deposition rates for sulfur dioxide under winter- and summer-like conditions, one of the more relevant data sets is that of Summers (1977). For the rainout and snowout of sulfur dioxide, he obtained the following equations:

$$\Lambda_{\text{rainout}} = 3 \times 10^{-5} \text{ J sec}^{-1} \quad (7)$$

$$\Lambda_{\text{(dry)snowout}} = 10^{-6} \text{ J sec}^{-1}. \quad (8)$$

Taking into account representative rainfall rate data for various types of precipitation, and using Equations (7) and (8), Summers estimated the following range of values for Λ : light, moderate and heavy snow - $10^7\Lambda$ = 1, 5 and 25 respectively; moderate rain or showers, heavy rain or thunderstorms - $10^4\Lambda$ = 3 and 7.5 respectively. Clearly, for regions where the wintertime precipitation largely consists of dry snow (- as for much of Central Canada), the above results indicate a seasonal change in the wet scavenging rate of two or three orders of magnitude, which cannot be ignored in air quality modelling work. It is interesting to note - see Figure 1 - that the snowfall drops sharply south of the states of Pennsylvania, Ohio, Indiana and Illinois.

Other areas, such as the east and west coasts of Canada and much of the United States, receive appreciable amounts of wet snow and cold rain during the winter months. Fortunately, our understanding of the physical and chemical processes involved in sulfur dioxide wet deposition is sufficiently complete to allow estimates of the resulting seasonal deposition changes. Summers (1977) has argued that, because of the large sweep-out area associated with wet snow (which should have a collection efficiency E similar to that of rain), its scavenging coefficient should be somewhat greater than for rain at an equivalent rainfall rate (-he recommends a value approximately twice as great). On the other hand, for sulfur dioxide removal by rain droplets, several relevant theoretical investigations are available, which are based on the acceptable assumption that, for purposes of regional transport modelling, the sulfur dioxide in the air is in equilibrium with that in the rain (-see, for example, Hales and Dana, 1979a; Barrie, 1981). Figure 2, for example, taken from Barrie (1981), shows the predicted functional dependence of W, for sulfur dioxide, on rainwater pH and temperature. In going from 25 to 0°C, for example, W increases roughly by a factor of four. It should be noted that in much of N. Eastern America precipitation tends to be somewhat more acidic in summer than winter (e.g., Pack and Pack, 1979), so from Figure 2 the expected difference between the winter- and summer-time values of W for rain would be even greater than predicted on the basis of temperature alone. For example, for a unit increase in pH and a change in temperature from 25 to 0°C, which might be representative of the seasonal variation at some of the stations in the N.E. U.S.A. (Pack and Pack, 1979), the predicted increase in W is roughly one order of

magnitude. Limited experimental measurements of sulfur dioxide in precipitation support the above arguments (Hales and Dana, 1979). As a matter of interest, Figure 3 gives the N. American percentage frequency of hourly temperatures below $0^{o}C$ in January and $10^{o}C$ in July, and above $10^{o}C$ in January and $21^{o}C$ in July, from which the importance of the above temperature effect can be estimated.

For the case of particulate sulfur, very few data are available on which to base conclusions about winter- summer-time differences in wet deposition, and our understanding of the details of rain and snow interactions with particles is not nearly as complete as for the case of sulfur dioxide. The existing theories are of little help if one wants to go beyond order-of-magnitude washout rate estimates. The only work where a direct experimental comparison of rain and snow scavenging coefficients has been made, for particles comparable in size to sulfates, is that of Graedel and Franey (1975). They found below-cloud Λ values for snow to be twenty times or more than those for rain. However, Graedel and Franey's interpretation of their data has been questioned by Slinn (1976).

Knutson and Stockham (1977) have developed equations for the scavenging coefficient of snow from laboratory study results with single snowflakes, which usually agreed with available field data to within a factor of three. For particles of about 0.5 microns in diameter, and a precipitation intensity of 1 mm h^{-1}, their model predicts scavenging coefficients in the range of $0.5 - 1.0 \times 10^{-3}$ sec^{-1}, depending on the type of snow. These values may be compared to some data on rain scavenging coefficients for particles of similar size compiled by McMahon and Denison (1979). Table 1 is abstracted from their Table 9. No attempt was made at a critical evaluation of the methods used to arrive at the scavenging coefficients in this Table. However, the last value shown (for 0.3 - 0.5 micron particles) was obtained by Graedel and Franey (1977) (-McMahon and Denison, in their Table 9, have incorrectly labelled Graedel and Franey's data as being obtained from snowfalls), and if we accept Slinn's criticism of their methodology (see above) and reject their data point, all we can say is that, for a particle size which might be representative of sulfates, most of the available data suggest that below-cloud rain and snow scavenging coefficients should be about the same order-of-magnitude for comparable rainfall rates. The scanty relevant data on washout ratios support the above conclusion (see McMahon and Denison, 1979) although in this case both within- and below-cloud processes are involved. Scott (1981) has recently presented data on washout ratios of sulfates in snowstorms, which fall within about the same range of values as has been observed for a number of other substances in rain. However, he found that the washout ratio is strongly dependent on the microphysical processes of precipitation growth, W values being 10 to 50 times higher when abundant cloud water was available (and snowflake growth was primarily through collection of supercooled droplets) than when negligible liquid water was detected in the clouds (and growth was primarily by vapour deposition on snowflakes).

2.1.3 Summary

To summarize the above discussion on wet deposition of sulfur compounds: it would seem that for sulfur dioxide, the washout coefficient for both within- and below-cloud processes can show a strong seasonal dependence (order-of-magnitude or more), even after seasonal variations in precipitation rate are taken into account, because of temperature and pH effects on the solubility, and the low uptake of the gas by ice crystals.

The available data on particulate sulfur wet scavenging is too meager to allow any definite conclusions about seasonal differences. All one can say is that below-cloud scavenging coefficients for rain and snow seem to be of the same

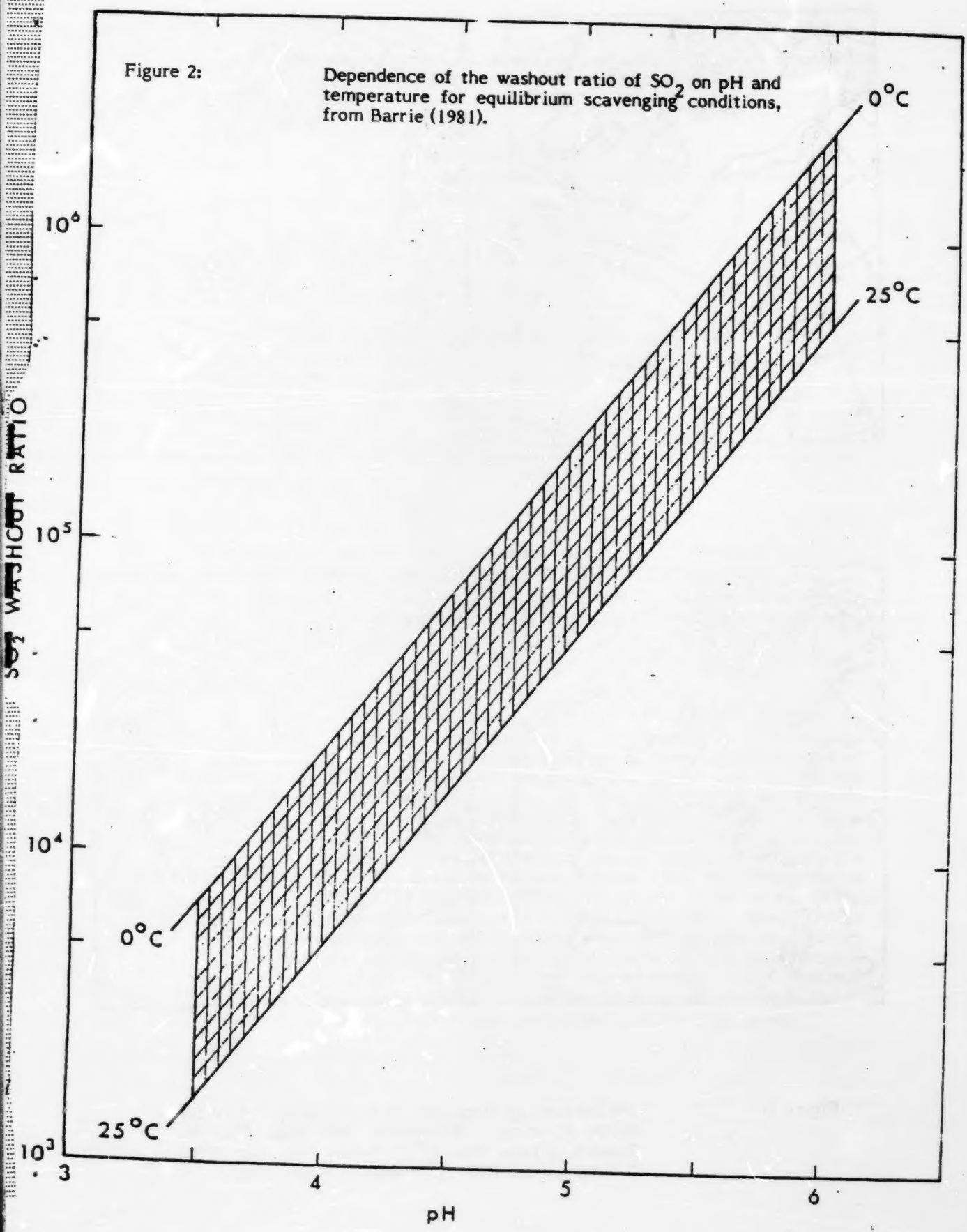
order-of-magnitude. However, rates of in-cloud processes depend strongly on the specific mechanisms involved (Scott, 1978; 1981), and seasonal variations in storm type could result in corresponding changes in scavenging rates of an order-of-magnitude or more, but more data are needed to substantiate or disprove this speculation.

Table 1: Field Measurements of Rain Scavenging Coefficients of Particles Expected to be Mainly in Submicron Size Range.

Source of Data	$10^5 \Lambda$ (s^{-1})	Comments
Kalkstein et al. (1959)	2	SO_4 washout.
Makhonko(1964)	1	Fission products washout.
Bakulin et al. (1970)	3	Pb washout from thunderstorm.
Burtsev et al. (1970)	$15\ J^{0.5}$	0.2 um particle washout.
Greadel and Franey (1977)	18	0.3 - 0.5 um particle washout.

Figure 1: Average annual distribution of snowfall in North America (cm) from Findlay (1980).

Figure 2: Dependence of the washout ratio of SO_2 on pH and temperature for equilibrium scavenging conditions, from Barrie (1981).



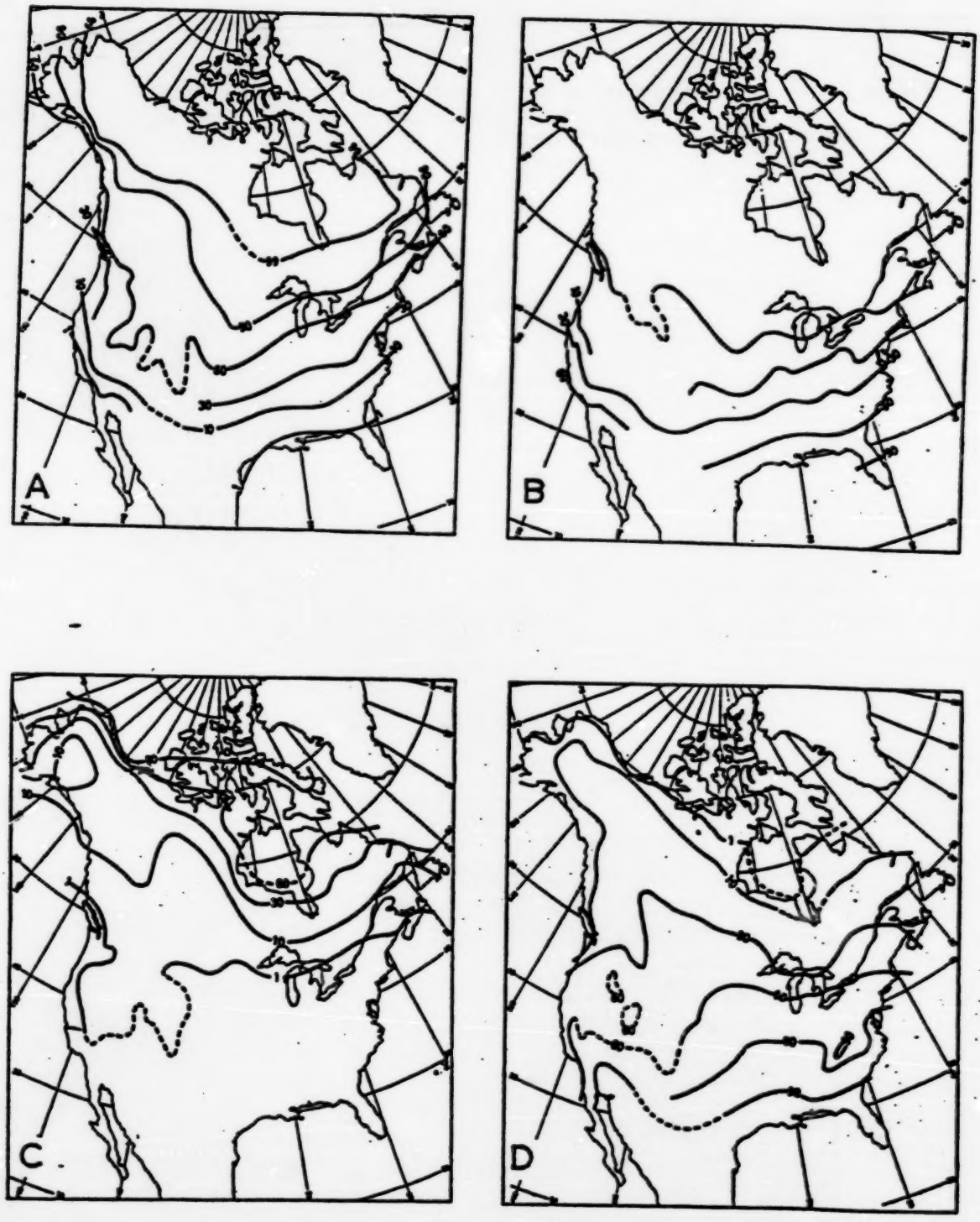


Figure 3: The percentage frequency of hourly temperature for North America: A-January, less than 0°C; B-January, greater than 10°C; C-July, less than 10°C; D-July, greater than 21°C (after Rayner, 1961).

2.2 Dry Deposition

The dry deposition rate of gases and particles to the earth's surface has usually been parametrized using a deposition velocity v, defined by the equation

$$v = Mc^{-1} \quad (9)$$

where
M = the flux of material
C = the ambient concentration at a particular height

and v (which is a function of height) refers to the same level as the concentration measurement.

2.2.1 General Considerations

To better understand the role of different factors which affect the deposition velocity, it is convenient to work in terms of resistances to transport. The total resistance r_t, defined as the reciprocal of v,

$$r_t = v^{-1} \quad (10)$$

can be broken down into an aerodynamic resistance r_a and a surface resistance r_s:

$$r_t = r_a + r_s \quad (11)$$

The surface resistance can be further split into a resistance due to a (usually thin) stagnant air film adjacent to the absorbing surface, r_b, and an actual resistance to transport within the surface (for plants, this is largely the canopy stomatal resistance), r_c (Wesely and Hicks, 1977; Chamberlain, 1979):

$$r_s = r_b + r_c \quad (12)$$

The magnitude of the aerodynamic resistance r_a is largely governed by atmospheric turbulence in the boundary layer, which in turn depends on factors such as wind speed, atmospheric stability, and characteristics of the surface (i.e. the surface roughness). There are well-known micrometeorological formulae relating r_a to meteorological and surface parameters (see, e.g., Garland, 1978; Wesely and Hicks, 1977). The value of r_a decreases as the wind speed and surface roughness increase, and also depends to a certain extent on the atmospheric stability, although the latter dependence only seems to become marked when the atmosphere is very stable - e.g., for Pasquill stability category F (Sheih et al., 1979). Because of the dominant influence of turbulent diffusion, r_a should be the same for both particles and gases, except where the particles are so large that gravitational settling plays an important role in the deposition process (e.g., Sehmel, 1980). In view of the above considerations, seasonal variations in meteorology and surface characteristics will obviously change the aerodynamic resistance to transport of both particles and gases.

The stagnant film resistance, r_b, also depends to a certain extent on the same factors as r_a, since surface drag forces and the intensity of atmospheric turbulence will determine the average thickness of the film and also the intrusion of turbulent eddies into the film. However, because of the importance within the film of molecular diffusion for gases, and Brownian diffusion and impaction for aerosols, r_b is also strongly dependent on the characteristics of the material under consideration - in particular, the diffusivity of gases and the particle size distribution of aerosols (see, for example, Wesely and Hicks, 1977; Sehmel, 1980). As with r_a, it can be seen that seasonal variations in meteorological and surface factors can lead to corresponding variations in r_b. In addition, if for particles there are appreciable seasonal changes in the size distribution, potentially large changes in r_b could result (e.g. Sehmel, 1980; Ibrahim et al., 1980).

As implied by its definition, for a given substance r_c depends only on the characteristics of the surface. For particles, probably for lack of reliable information to the contrary, it has sometimes been assumed that r_c is equal to zero (e.g. Ibrahim et al., 1980; Sievering, 1979 a). For gases, r_c depends on the properties of the gas (- mainly the solubility in water (Hill, 1971) and molecular diffusivity (Wesely and Hicks, 1977)) and the absorbing surface. For surfaces covered by vegetation, r_c depends on the nature, and state of growth and condition, of the plant in question, the latter being influenced by the water availability, solar radiation level, and air temperature, among other things. Obviously, seasonal changes in the surface coverage will lead to corresponding changes in r_c.

For a more detailed discussion of the individual resistances which determine the overall magnitude of the deposition velocity, and the factors affecting them, see Wesley and Hicks (1977), Shieh et al. (1979), Chamberlain (1979) and Sehmel (1980).

2.2.2 Experimental Results

Several authors have recently presented compilations of experimental data on the deposition velocities of gases and particulates, which are of value in assessing the effects of seasonal variations on v (see Garland, 1978; McMahon and Denison, 1979; Chamberlain, 1979; Sehmel, 1980).

For the case of sulfur dioxide, a reasonably consistent picture emerges. For a wide range of surfaces, including vegetation, water, and soils, the deposition velocity has been found to be typically in the range 0.4 to 0.8 cm s^{-1}. Garland (1978) rationalizes the above result by pointing out that in general, there is a counter-balance between the aerodynamic and surface resistance terms (r_a and r_s in Equation (11)). For relatively smooth surfaces, r_s has been found to be rather small, and uptake is largely determined by r_a. On the other hand, surfaces with taller vegetation, such as wheat and forest, exhibit a higher r_s, which counteracts the reduced r_a. Of course, there are exceptions to the above generalizations: for example, much higher v values than indicated above may apply to wet or snow-covered forests (Chamberlain, 1979). However, it would seem that such exceptions have only marginal relevance when seasonal variations are being considered (unless, for example, the percentage of the time that a forest is wet changes significantly, due to seasonal changes in precipitation).

It is interesting to compare measured deposition velocities to snow with the 0.4 to 0.8 cm s^{-1} range in v noted above, which is assumed to be representative of surfaces for most of the year other than winter. Table 2 lists the available data for sulfur dioxide depositon to snow surfaces. The values measured generally tend to be lower than 0.4, although a "representative" v of 0.1 cm s^{-1} for snow, as suggested by Husar et al. (1978b), would seem to be too low, except for very stable atmospheric conditions.

The above results suggest that seasonal variations in sulfur dioxide dry deposition velocities should be relatively modest - certainly less than the order-of-magnitude changes expected for wet deposition. It seems that for the wintertime, at least in Canada and the northern United States, dry deposition velocities of sulfur dioxide should be somewhat lower than in the summer, due to the larger proportion of the surface covered by snow and dead vegetation. In this connection, it is interesting to compare some estimates of v for the summer (June - August) and winter (December-February) months in Ontario, made using the methods of Shieh et al. (1979). Surfaces were characterized according to their classification, and values of surface roughnesses and resistances were taken from their Table 3. Information on the frequency of occurrence of Pasquill stability classes at 22 stations in Ontario was provided by the Atmospheric Environment Service. Calculated seasonal average depositon velocities are shown in Figures 4 and 5. A comparison of these figures supports the expectation that, for sulfur dioxide, seasonal changes in v should not be large.

The picture for sulfate particulates is much more confusing, because of the current controversy regarding depositon velocities of particles in the 0.1 - 1.0 micron size range (where most of the sulfate mass is expected to occur). Theoretical predictions (see, for example, Sehmel and Hodgson, 1978; Ibrahim et al., 1980) indicate that, for this size range, $(r_a + r_b)$ should be generally larger than 10 s cm^{-1} (i.e., v should be no greater than 0.1 cm s^{-1}). Available experimental data on depositon velocities of sulfates, or other substances such as lead (which are expected to be in a similar size range) are shown in Table 3. It would seem that for relatively smooth surfaces, such as snow, water, or filter paper, the deposition velocity is about 0.1 -0.2 cm s^{-1}, or in some cases so small that the removal of particles is countered by surface emissions (i.e., the effective deposition velocity is negative). For rougher surfaces and vegetation there is little data, but values ranging from less than 0.1 to about 1.0 cm s^{-1} have been reported, including a number of negative values. For such surfaces, Sheih et al. (1979) have proposed sulfate deposition velocities comparable to those for sulfur dioxide. However, at present, because of the large uncertainty in v for particulate sulfate, little can be said about seasonal variations in this parameter.

2.2.3 Summary

To summarize: there are several theoretical reasons why dry deposition velocities for both gaseous and particulate sulfur could have a significant seasonal variation. However, for sulfur dioxide, this variation is probably rather small, as far as long-range transport modelling is concerned. Summertime values have been typically observed to be in the range 0.4 to 0.8 cm s^{-1}. Wintertime observations (Table 2) indicate a "representative" range of 0.1 to 0.4 cm s^{-1}. The few available data suggest

that this latter range is also representative of the deposition of particulate sulfates to smooth surfaces. However, for rougher surfaces and vegetation, the picture is so confusing at present that little can be said concerning seasonal variations in the particulate dry deposition velocity.

Table 2: Deposition Velocities of Sulfur Dioxide to Snow.

Reference	v cm s^{-1}	Comments
Whelpdale and Shaw (1974)	1.6	Lapse
	0.52	Neutral
	0.05	Stable
Garland (1976)	0.10 - 0.17	Ice - laboratory experiments; r_s 5 s cm^{-1}.
Dovland and Eliasen (1976)	$\sim$0.1	Low wind speed, stable atmosphere; r_s 5 s cm^{-1} (Garland, 1976).
Barrie and Walmsley (1978)	0.25 $\pm$ 0.20	Determined from simultaneous deposition and concentration measurements during a pollution episode.
	0.3 - 0.4	Determined from sulfur accumulation by snow and ambient concentrations calculated with a dispersion model.

Table 3: Deposition Velocities for 0.1 - 1.0 Micron Particles.

Reference	v cm s^{-1}	Comments
Cawse (1976)	0.2 -<0.7	Vanadium on filter paper at 1.5 m.
	<0.1 -<0.6	Arsenic on filter paper.
Dovland and Eliasen (1976)	0.16	Lead on snow, stable atmosphere.
Garland (1978)	<0.1	Atmospheric sulfate over grass.
Droppo (1979)	0.1, 0.27	Sulfates over arid vegetation.
	Negative (surface source)	Sulfates, daytime, non-arid vegetation.
Sievering (1979)	<0.5	Estimated annual average over Lake Michigan, submicron atmospheric aerosols.
Sievering et al. (1979)	0.2 ± 0.16	Atmospheric sulfate over L. Michigan, stable atmosphere.
Wesley and Hicks (1979)	~1	Submicron particles to grass.
	Negative (surface source)	Nighttime, pine plantation, senescent maize.
	Negative	Snow, and cold, wet, bare soil.
Everett et al. (1979)	1.4	Atmospheric particulate sulfur over slightly rolling grassland.
Ibrahim et al. (1980)	0.1 - 0.2	Bimodal ammonium sulfate aerosol over snow. (These results are complicated by the fact that, although over 90% of the total mass was in the 0.7 micron mode, most of the material actually deposited came from the 10 micron mode).

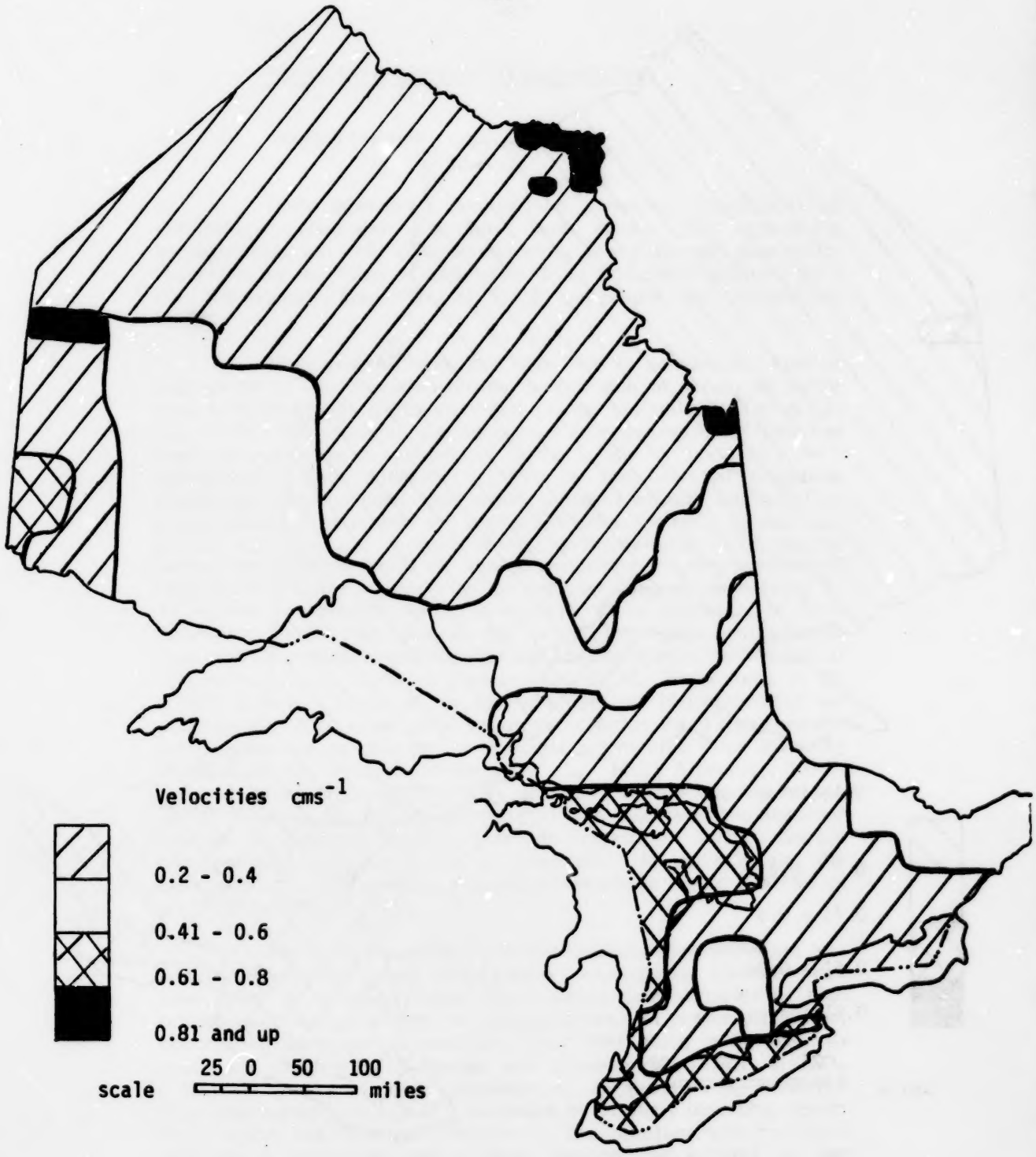


Figure 4: Deposition velocities of SO_2 for June-August.

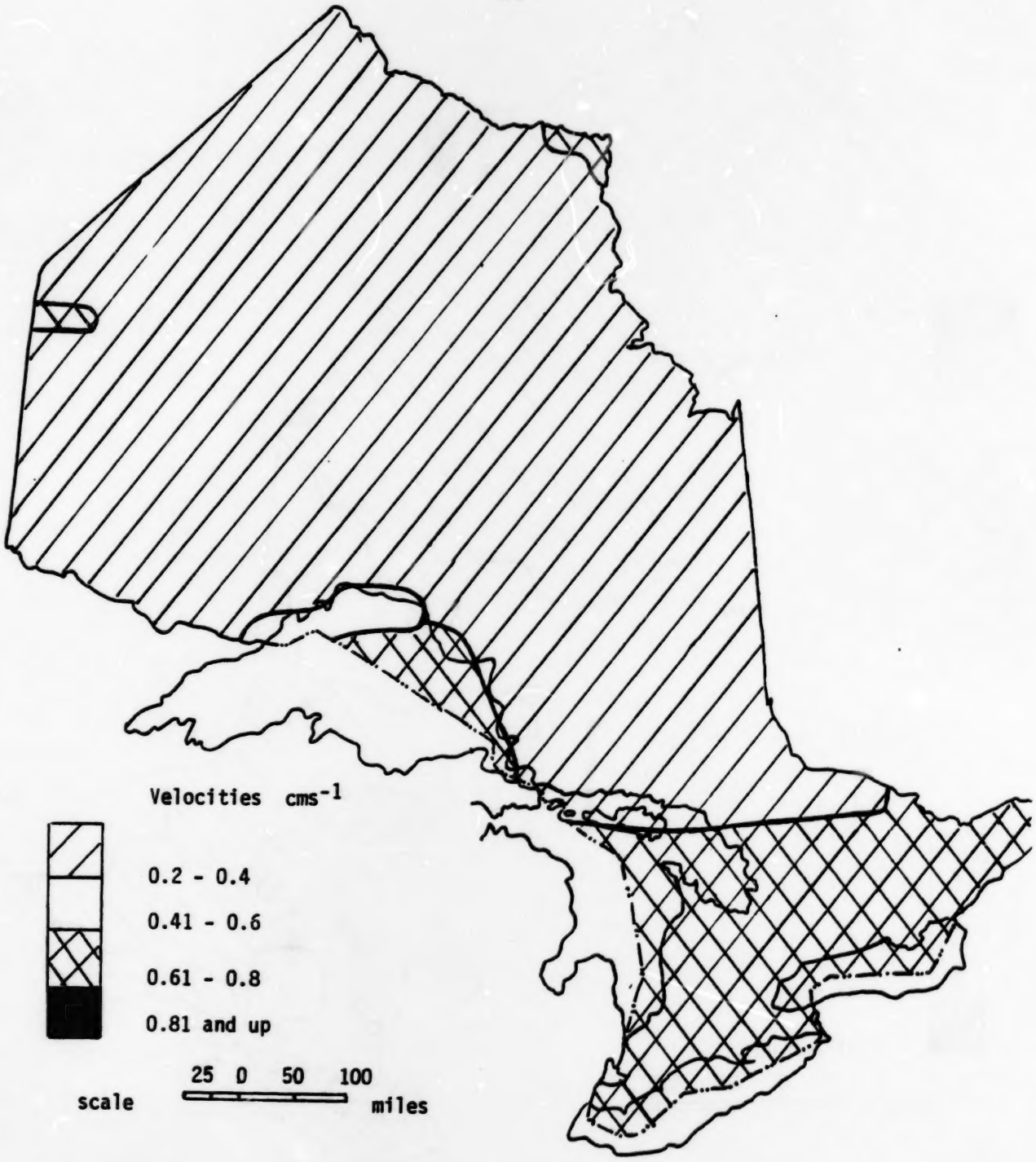


Figure 5: Deposition velocities of SO_2 for December-February.

3. Atmospheric Chemical Transformations

3.1 General Considerations

Both laboratory studies and computer simulations of atmospheric chemical reactions have shown that gas-phase homogeneous, as well as heterogeneous, reactions are potentially important for oxidation of sulfur dioxide to sulfates in polluted air - see, for example, Calvert et al. (1978) and Beilke and Gravenhurst (1978).

Homogeneous reactions can lead to conversion rates as high as 4% h^{-1} in the summertime, largely due to attack of sulfur dioxide by hydroxyl, hydroperoxy and alkylperoxy radicals (Calvert et al., 1978). The seasonal dependance of homogeneous reactions has been discussed by a number of authors, and is reasonably well understood. Thus Altshuller (1979), on the basis of computer modelling studies, found that while seasonal effects are small at lower latitudes, at middle and higher latitudes the ratio of summer-winter noontime and average diurnal photochemical rates can be large: for example, at 35°N, summer noontime and average diurnal rates are 4-5 times greater than the corresponding winter values. At 55°N, the summertime values are 16-20 times greater. In fact, Altshuller finds that during the winter months, homogeneous oxidation reactions cannot account for any significant conversion of SO_2 to sulfate at latitudes greater than 45°N. Bottenheim et al. (1977), in their study of seasonal effects on photochemical air pollution at 60°N, have come to similar conclusions. These results are largely due to changes in available ultraviolet solar intensity (Nieboer et al., 1976; Bottenheim et al., 1977; Altshuller, 1979), although temperature effects may also play a role (Carter et al., 1979). Table 1, taken from Altshuller (1979), illustrates the expected effects of season and latitude on noontime sulfur dioxide homogeneous oxidation rates in clean air. In polluted air, the corresponding rates could be a factor-of-two or so higher (Calvert et al, 1978; Altshuller, 1979).

Heterogeneous sulfur dioxide oxidation processes are less well understood than their homogeneous counterparts. Oxidation can take place in droplets, liquid films surrounding particles at high relative humidity, or on dry particle surfaces. At present, the most important heterogeneous reactions which take place in the aqueous phase are thought to be (Beilke and Gravenhurst, 1978): (1) SO_2 oxidation by O_2 in the presence of catalysts (e.g., dissolved transition metals); and (2) SO_2 oxidation by strongly oxidizing agents (e.g., ozone and hydrogen peroxide). The reaction with hydrogen peroxide in particular has recently excited the interest of the scientific community, due to its potential atmospheric importance (-see, for example, Penkett et al., 1979; Dasgupta, 1980). To date, there has been no clear demonstation that SO_2 - dry particle reactions are of atmospheric significance, except possibly in smokestack plumes close to the chimney (where concentrations are

relatively high). For example, Britton and Clark (1980) have recently reviewed past work on heterogeneous SO_2 reactions on dry particles, and have presented the results of some of their own studies with soot and SO_2/NO_2 mixtures. In their conclusions, they state: "From the point of view of the overall SO_2 oxidation process in the atmosphere the heterogeneous reactions on soot or other particles play a negligible part compared to either photochemical or droplet phase mechanisms...". Therefore, such processes will not be considered further here.

It was noted above that, for homogeneous processes, large seasonal changes may be theoretically expected in the oxidation rate, depending on the latitude. The picture is not as clear for heterogeneous reactions. It has been theorized (e.g., Foster, 1969; Freiberg, 1974) that the oxidation rate involving trace metal catalysts should be increased at high ambient ammonia concentrations and relative humidities, both of these factors leading to lower solution acidity and hence higher sulfite ion concentrations (- sulfite ions are thought to be the species actually oxidized to sulfate by dissolved O_2). Lower temperatures may also promote oxidation by hydrogen peroxide or trace metal catalysts (Penkett et al., 1979; Freiberg, 1974). Thus, seasonal variations in all these factors - e.g., lower wintertime temperatures and ambient ammonia concentrations - could potentially effect on the conversion rate. These effects are difficult to predict. For example, Middleton et al. (1980) have carried out a modelling study into the relative importance of various urban sulfate aerosol production mechanisms, including photochemical reactions followed by sulfuric acid vapour condensation, and catalytic as well as non-catalytic heterogeneous oxidation. They conclude that the dominant mechanism for sulfate production can depend on the season and time of day. During the daytime in summer, photochemical reactions/sulfuric acid vapour condensation are the most important, followed by liquid phase oxidation by hydrogen peroxide. At night, however, catalytic and non-catalytic oxidation mechanisms on the wetted aerosol surface become important. In the winter, most of the daytime SO_2 oxidation is predicted to take place by reactions with hydrogen peroxide in droplets, at overall rates comparable to those in the summer. However, the above conclusions are based on a large number of assumptions about reaction mechanisms and model input conditions, and should not be regarded as final. For a better assessment of winter/summertime differences in atmospheric chemical transformation rates, the results of actual field studies were consulted (see below).

3.2 Experimental Results

A large number of field investigations have been carried out into the oxidation of sulfur dioxide in urban, industrial and power plant plumes. Since, on the basis of our present understanding of atmospheric chemistry, there is a fundamental difference between urban plumes and those from strong point sources (- at least, before the latter have been well-mixed into the "background" air), the two will be considered separately. Also, in view of the suggested

importance of latitude when considering winter and summertime differences in photochemical processes (see above), the geographic location of each experiment will be noted whenever possible in the following discussion.

Newman (1980) has recently summarized the available results on atmospheric oxidation of SO_2 from power plant and smelter plume studies. Table 5 is largely based on the most relevant references taken from his paper. In preparing this table, we have concurred with Newman in that some of the early, and often-cited, studies of plume oxidation, such as that by Gartrell et al. (1963) and Stephens and McCaldin (1971), are probably flawed, and the results are unreliable. Rather we have emphasized those particular more recent studies which have a direct bearing on seasonal effects on the plume oxidation rate.

An inspection of Table 5, and the references cited therein, leads to the following general conclusions about the sulfur dioxide oxidation rate in power plant and smelter plumes:

1. The "dry" oxidation rate is usually small - no more than a few percent per hour.

2. Although there is still a debate about the relative importance of homogeneous gas-phase reactions, and heterogeneous processes involving catalytic plume aerosols, most of the evidence suggests the former are important, and can lead to SO_2 transformation rates of up to about 4% h^{-1}. Heterogeneous reactions may dominate near the point of emission where the particle concentration is high, or under high humidity conditons.

3. Under conditions where homogeneous photochemical reactions are not expected to be significant (e.g., during the night or early morning, or during the winter at far northern locations), conversion rates have been observed to be small - generally, well below 1% h^{-1}.

4. Temperature or relative humidity may or may not have an effect on the conversion rate (compare Lusis et al., Forrest et al., Chan et al., Garber et al., with Eatough et al., Dittenhoefer and De Pena in Table 5). However, the degree of plume dilution due to atmospheric mixing is certainly important (Wilson and Gillani, 1980).

It must be emphasized that the above summary represents a considerable simplification of what happens during atmospheric SO_2 oxidation in chimney plumes, and a more rigorous treatment would require separate consideration of each point source, including the composition of the emissions as well as that of the background air into which the plume is mixing.

Before drawing any conclusions on the seasonal dependence of the SO_2 transformation rate from the above data, consider the corresponding data obtained from studies of urban plumes. Although urban plume data are more relevant to long-range transport modelling than chimney plume data, which generally have represented conditions within the first hour or two of emission, they are also more difficult to interpret. To extract the oxidation rate from the data, assumptions have to be made about other atmospheric processes such as air parcel dilution and dry deposition (see, for example, Alkezweeny and Powell, 1977). This should be kept in mind when evaluating the urban plume results.

Alkezweeny (1980) has summarized the available data on SO_2 oxidation in urban plumes, and the results in Table 6 are largely taken from his paper. An inspection of this table suggests that:

1. "Dry" oxidation rates in urban plumes are somewhat higher than those in chimney plumes (- at least, before the latter have been mixed into the background air), possibly by a factor-of-two or more.

2. Although homogeneous photochemical processes are important (Alkezweeny, 1980), heterogeneous mechanisms may play a greater role in urban than in power plant and smelter plumes (close to the source). Thus, whereas power plant and smelter plume data suggested very low oxidation rates under conditions where homogeneous processes are not expected to be significant, the urban plume data in Table 6 indicate that quite high oxidation rates have been observed in the wintertime at latitudes greater than 45° N (- see, for example, the results of Benarie et al., Elshout et al., Prahm et al., and Smith and Jeffrey). Alkezweeny (1980) also has noted in his own data that high oxidation rates seem to be associated with high aerosol loadings.

3. There is some indication that temperature may have an effect on the conversion rate, although, as with chimney plume studies, the information is conflicting (compare Benaire et al. with Meszaros et al.). There is also confusion on the correlation of conversion rate and relative humidity (compare Benaire et al. with Smith and Jeffrey).

3.3 Summary

The above experimental results make it difficult to draw any firm conclusions on the seasonal variation of SO_2 oxidation rate. Perhaps this much can be said: during the summer months, photochemical processes are important, and both point source and urban plume data indicate daytime "dry" rates of several percent per hour (a summertime diurnal average of 1 - 2% h^{-1} might be suitable for long-range transport modelling, although some of the urban plume data suggest rates several times greater than this). In

the winter, it is not clear what one should expect. The chimney plume data, most of which may be of questionable relevance to long-range transport modelling because of high pollutant concentrations, indicate oxidation rates generally considerably less than 0.5% h^{-1} at latitudes where photochemical reactions should not be contributing appreciably. On the other hand, the limited urban plume data suggest a greater role of heterogeneous processes, and therefore appreciable oxidation rates, but at the same time they have been derived with more assumptions about the history of the air parcel, and are therefore more open to criticism (- see, for example, Forrest et al., 1979b). It must be concluded that at present the available data is too conflicting to draw any firm conclusions about the seasonal dependence of the SO_2 oxidation rate.

There is one more factor which makes any conclusions difficult at the present time - viz., the possibly important role of clouds (both precipitating and fair weather) in converting SO_2 to sulfates. Recently, there has been a considerable amount of speculation that in-cloud processes contribute significantly to SO_2 oxidation (see, for example, Hegg and Hobbs, 1978; Hales and Dana, 1979b; Newman, 1979; McNaughton and Scott, 1980; Scott, 1980). If this can be proven experimentally (work is currently in progress by several groups of researchers), then expected seasonal variations in SO_2 transformation could increase considerably, especially in areas where clouds consist largely of dry ice crystals in the winter (and hence have very low chemical transformation potential, as compared to summertime conditions).

Table 4: Effects of Month and Latitude on Photochemical Homogeneous Oxidation of Sulfur Dioxide in Clean Air (Noontime rates in % h^{-1} from Altshuller 1979)

	Latitude (°N)						
Month	5	15	25	35	45	55	65
January	1.81	1.10	0.61	0.26	0.08	0.01	0.01
February	1.81	1.21	0.74	0.32	0.13	0.04	0.01
March	2.06	1.55	1.01	0.48	0.21	0.09	0.03
April	2.01	0.79	1.36	0.73	0.35	0.17	0.07
May	1.82	1.68	1.48	1.01	0.58	0.30	0.16
June	1.81	1.72	1.56	1.22	0.74	0.42	0.25
July	1.78	1.80	1.58	1.30	0.88	0.52	0.31
August	1.86	1.78	1.61	1.31	0.82	0.45	0.26
September	1.91	1.68	1.50	1.15	0.76	0.34	0.17
October	1.79	1.54	1.29	0.84	0.39	0.17	0.06
November	1.56	1.33	0.98	0.48	0.19	0.06	0.02
December	1.58	1.16	0.74	0.33	0.11	0.02	0.01

Table 5: Conversion of SO_2 in Power Plant and Smelter Plumes

Source	SO_2 Oxidation Rate (% h^{-1})	Comments
Forrest and Newman (1977)	$\lesssim$1.5	- four coal-fired power plants (30° - 40°N) - no correlation could be found between conversion and temperature (10 - 25°C), humidity or time of day.
Husar et al. (1978a)	1 - 4 (noontime) $\lesssim$0.5 (night)	- St. Louis (38°N) - power plant - photochemistry may be the dominant mechanism.
Lusis et al. (1978)	1 - 3 (June, noon and p.m.) $\lesssim$0.5 (winter, or summer early a.m.)	- Fort McMurray (57°N) - power plant - evidence of photocemical activity during relatively high conversion rates - temperature varied from -13 to 23°C.
Dittenhoefer and de Pena (1979)	0 ($\ll$65% RH) $\sim$1 (65 - 90% RH) 2 - 6 (90% RH)	- Pennsylvania (41°N) - power plant - evidence that both gas phase and aqueous phase oxidation are important.
Forrest et al. (1979a)	$\lesssim$ 2	- Tarpon Springs, Florida (28°N) - oil-fired power plant - no correlation was found between individual meteorological parameters and extent of oxidation, although higher conversions were observed in August than in February.
Forrest et al. (1980)	0.1 - 0.8 (night, early a.m.) 1 - 4 (late a.m. and afternoon)	- Cumberland coal-fired power plant (35°N) - reactions were correlated with solar radiation.
Garber et al. (1980)	$\lesssim$1	- Northport oil-fired power plant (41°N) - a wide range of meteorological conditions were examined. The data suggest a weak positive correlation of conversion rate with temperature, water partial pressure and insolation.

Table 5 (continued)

Source	SO_2 Oxidation Rate (% h^{-1})	Comments
Hegg and Hobbs (1980)	0 - 5.7	- five coal-fired power plants, W. and Midwest U.S.A. - various times of year - evidence of photochemical reactions. Conversion depended on u.v. light intensity.
Gillani et al. (1980)	rate = 0.03 R.H.O_3 R = solar radiation H = mixing height O_3 = background ozone	- plumes from Labadie, Cumberland and Johnsonville power plants - for dry conditions only.
Chan et al. (1980)	< 0.5	- Sudbury smelter plume (47°N) - no correlation of rate with temperature, relative humidity.
Eatough et al. (1980)	<0.5 to 6	- Western U.S. smelter and power plant plumes - positive temperature dependence of oxidation rate; data are consistent with a homogeneous mechanism.

Table 6: Conversion Rates of SO_2 in Urban Plumes.

Source	SO_2 Oxidation Rate ($\% h^{-1}$)	Comments
Benarie et al. (1972)	6 to 25	- Rouen (49^oN) - wintertime results - aerosol catalysis important; acid formation increases as temperature decreases.
Robert and Friedlander (1975)	1.2 to 13	- Los Angeles (34^oN) - July, October.
Mezaros et al. (1977)	30	- Budapest (48^oN) - mainly June to September.
Alkezweeny and Powell (1977)	10 to 14	- St. Louis (38^oN) - August.
Alkezweeny (1978)	8 to 12	- St. Louis (38^oN) - summertime
Breeding et al. (1976)	5 to 32	- St. Louis (38^oN) - October, April
Alkezweeny (1980)	1 to 5	- Chicago, Gary (42^oN) - summertime - conversion dominated by photochemical reactions.
Forrest et al. (1979b), Chang (1979)	4	- St. Louis (38^oN) - Flight Da Vinci II, June.
Alkezweeny (1980)	0, 6.8	- Milwaukee (44^oN) - measurements on two days in August.
Elshout et al. (1978)	0.6 to 4.4	- Arnheim, Amsterdam (52^oN) - January to March.
Prahm et al. (1976)	1.1	- Faroe Island and British Isles (50 to 60^oN) - February.
Smith and Jeffrey (1975)	0 to 3	- British Isles (52 to 56^oN) - mainly September to November - relative humidity is important.
Lavery et al. (1979)	0.7	- Ohio Valley (40^oN) - August.

4. Nitrogen Oxides Deposition and Chemistry

The atmospheric chemistry and deposition of sulfur oxides has in the past received considerably more attention than that of nitrogen oxides. However, the recognition that the latter are important precursors of acid deposition, and that emissions of nitrogen oxides will grow considerably more than those of sulfur oxides in the coming two decades (U. S. - Canada Research Consultation Group on LRTAP, 1979), has recently led to a substantial increase in the level of research devoted to the atmospheric nitrogen compounds. Nevertheless, at present relatively little has been published on deposition and chemical transformation rates of nitrogen oxides. Most of the information we are aware of is summarized in the present chapter.

Since many of the general physical and chemical considerations regarding deposition and transformation (outlined in Sections 2.1.1, 2.2.1 and 3.1) also apply to nitrogen oxides, some speculation is possible in the absence of field data regarding their transformation and deposition rates and the seasonal dependence of these rates, but this has been kept to a minimum in the discussion below. The situation is somewhat more complicated than for the sulfur oxides, because the behaviour of more species must be considered. Thus, although anthropogenic emissions are primarily in the form of nitric oxide (NO), this coumpound is converted relatively rapidly to nitrogen dioxide (NO_2), nitric acid (HNO_3) and particulate nitrates, and peroxyacetyl nitrate (PAN) (-see, e.g. Spicer, 1979; Spicer et al., 1980). The chemical reactions and atmospheric deposition of each of these species will be considered separately below.

Nitric oxide has a very low solubility in water (Sherwood and Pigford, 1952). Since the rate of wet deposition, especially under the "equilibrium scavenging" conditions of relevance to long-range transport (Hales, 1978), is directly dependent on the solubility of the gas under consideration, the wet scavenging coefficient of NO is also expected to be low. As far as dry deposition is concerned, a number of investigators, working with different types of surfaces (see Table 7), have found the deposition velocity of NO to be very small - about one-tenth that for SO_2 over the same surface. Moreover, NO is oxidized to products fairly rapidly (in the order of a few hours) in the summertime, so the short lifetime and low wet and dry scavenging rates of this gas suggest that its contribution to deposition is small. Under wintertime conditions, at latitudes where photochemical reactions are of relatively little importance (see Section 3.1), the atmospheric lifetime of NO could be increased considerably, and the amount deposited by wet and dry removal processes could become important. However, no information is available on scavenging coefficients and deposition velocities of NO under these conditions, especially to snow surfaces.

Nitrogen dioxide is formed in the atmosphere mainly from the oxidation of NO by ozone and various free radicals (see, for example, Bottenheim et al., 1977; Calvert et al., 1978; Altshuller, 1979). It dissolves in water according to a fairly complex chemical

mechanism (Sherwood and Pigford, 1952), the overall reaction being

$$2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2.$$

As can be seen from the above reaction, the solubility of NO_2 will, like that for SO_2, depend on the acidity of the rain or cloud droplet, and laboratory experiments (Beilke, 1970) have shown the scavenging coefficient of NO_2 to be roughly one-quarter that for SO_2. Experiments on dry deposition rates of NO_2 to a number of surfaces have shown the deposition velocity of NO_2 to be roughly one-half that for SO_2 under comparable conditions (see Table 7). No wet and dry deposition data for NO_2 under wintertime conditions are available, especially to snow, but it seems reasonable that qualitatively the same differences in winter and summertime deposition behaviour will obtain as for SO_2.

As far as atmospheric chemistry is concerned, NO_2 is formed so quickly from NO under summertime conditions that, in mathematical modelling of long-range transport (where time steps of the order of several hours are involved in the calculations), as a first approximation emissions can probably be assumed to consist of NO_2 (i.e., the role of NO as an independent precursor species of nitrates and PAN can be neglected). This may not be true under nighttime conditions, or in the winter at northerly latitudes, but the scope of this report does not allow for more detailed speculation on this point.

Nitric acid is now thought to be one of the major products of NO emissions (e.g., see Spicer, 1979; Spicer et al., 1980). Under typical atmospheric conditions, it exists mainly in the vapour form. However, it is a highly soluble vapour (e.g., see Okita and Ohta, 1979), and potentially has a higher scavenging coefficient than that of SO_2 (no experimental data are available to verify this). There are also reports of unpublished experimental results which suggest that, unlike SO_2, HNO_3 is scavenged very efficiently by snow. Thus, even though no experimental data are available on wet removal rates of HNO_3, one can speculate that the seasonal dependence of Λ for this substance is probably smaller than that for SO_2 (and its overall magnitude is larger). Similarly, because of the apparently high reactivity of HNO_3 with all types of surfaces, it would seem reasonable to assume that the total resistance to mass transport is approximately equal to the aerodynamic resistance (i.e. $r_s \ll r_a$ in Equation (11)), and to use values calculated from micrometeorological theories (see, for example, Table 1 in Garland, 1978). This leads us to expect fairly small seasonal variations of the deposition velocity for HNO_3, probably smaller than those for SO_2.

Nitric acid can be formed by homogeneous reaction pathways, mainly by reaction with hydroxyl radicals, or in the droplet phase (Orel and Seinfeld, 1977; Middleton and Kiang, 1979). Homogeneous processes are relatively well understood compared to the heterogeneious ones, and are probably more important during the daytime in summer, and display a similar seasonal dependence to

those for SO_2 oxidation (see Section 3.1 and also Bottenheim and Strausz, 1980). Nitrogen oxides transformation rates of over 20% h^{-1} have been observed in urban plumes, most likely due to homogeneous reactions (Spicer, 1979), and power plant plume studies have also yielded nitrate formation rates several-fold those of sulfates (e.g., Forrest et al., 1980) which are consistent with a homogeneous reaction mechanism. Heterogeneous processes may be an important source of nitrates at night and in the winter (Middleton and Kiang, 1979), but too little reliable information is available on the chemistry involved to speculate on seasonal trends in the HNO_3 formation rate.

Particulate nitrates are probably formed by heterogeneous processes, and consist of a number of salts, with ammonium nitrate being one of the most important (Orel and Seinfeld, 1977; Middleton and Kiang, 1979). During the summertime, particulate nitrate concentrations are apparently relatively small compared to those of vapour phase nitric acid (e. g., see Spicer, 1979; Spicer et al., 1980; see also, Tang, 1980). During the winter, especially at northern latitudes, the reverse could be true, but due to difficulties involved in sampling HNO_3 and particulate nitrates separately, insufficient data are available to answer this question. Little can be said about the wet and dry deposition of nitrates, and its seasonal dependence. In the absence of experimental data, one might postulate a behaviour similar to that of sulfates. As far as chemical formation rates are concerned, some theoretical estimates suggest that wintertime rates for particulate nitrate may be considerably greater than those in the summer (Middleton and Kiang, 1979), but again, this result requires experimental verification.

The other major nitrate product to be considered is peroxyacetyl nitrate. This substance is stated by Hill (1971) as being "relatively insoluble", and Garland and Penkett (1976) found negligible PAN uptake rates by water in a wind tunnel. This suggests a relatively low value of the scavenging coefficient. The dependence of PAN solubility on the temperature, and the nature of its interactions with snow, are unknown; therefore, we will not speculate on the seasonal dependence of its wet scavenging rate. Some data are available on the dry deposition rate of PAN over a number of surfaces (Table 7), and, with the exception of water, the PAN deposition velocity seems to be about one-third that for SO_2. Again, due to lack of supporting data, speculation on the seasonal dependence of the PAN dry deposition rate is not possible.

As far as chemical formation rates are concerned, PAN is the product of photochemical reactions involving peroxyacetyl radicals and NO_2:

$$CH_3CO(O_2) + NO_2 \rightleftharpoons \text{PAN}.$$

The proportion of PAN and HNO_3 appearing in the irradiated, polluted air mixture depends on the level of hydrocarbons present in the mixture (Spicer et al., 1980), but limited field measurements

suggest that the two products can exist in comparable amounts (e.g., Spicer, 1979). Thus, PAN formation rates are expected to be several percent per hour under conditions where photochemical reactions are important. As far as the seasonal dependence of the PAN formation rate is concerned, one would expect it to be qualitatively similar to that resulting from the photochemical components of the sulfuric and nitric acid formation rates (see also Bottenheim et al., 1977), but it must be noted that the PAN formation reaction (see above) is reversible. The stability of PAN is a strong function of the temperature, and its atmospheric half-life at 275°K is about two orders of magnitude greater than that at 305°K (Hendry and Kenley, 1979). This will offset some of the seasonal dependence in net PAN formation rate due to photochemical reactions alone, but quantitative conclusions are not possible at present.

Table 7 summarizes the published data on wet and dry deposition rates that we are aware of. Also shown are some of the chemical transformation rates that have been measured in field experiments.

TABLE 7: Deposition and Chemical Transformation Rates for Nitrogen Compounds.

Compound	Parameter	Rate	Reference	Comments
NO_2	Λ	$\Lambda_{NO_2} \sim \frac{1}{4}\Lambda_{SO_2}$	Beilke (1970)	
	v	0.3-0.8 cms^{-1}	Judeikis & Wren (1978)	Soil, cement surfaces. For the same surfaces, deposition velocities for SO_2 were in the range 0.3-2.5 cms^{-1} with most values around 1 cms^{-1}.
		1.9 cms^{-1}	Sehmel (1980)	Alfalfa canopy, calculated from experiments of Hill (1971). For the same canopy, deposition velocity for SO_2 was 2.7 cms^{-1}.
NO	v	0.1-0.2 cms^{-1}	Judeikis & Wren (1978)	Soil, cement surfaces. See comments for NO_2 above.
		0.1 cms^{-1}	Sehmel (1980)	Alfalfa canopy. See comments for NO_2 above.
PAN	v	0.8 cms^{-1}	Sehmel (1980)	Alfalfa canopy. See comments for NO_2 above.
		0 0.25 cms^{-1}	Garland & Penkett (1976)	Water. Grass and soil surfaces.

TABLE 7 (continued)

Compound	Parameter	Rate	Reference	Comments
HNO_3	Conversion rate from NO_x	3 to 10 times SO_2 conversion rate	Richards et al. (1980)	Daytime measurements, Navajo generating station plume (Arizona); June-July and December.
HNO_3 and particulates nitrates	Conversion from NO_x	0.1 to 3% h^{-1} (nighttime) 3 to 12% h^{-1} (daytime)	Forrest et. al. (1980)	Cumberland coal-fired generating station, August. NO_x conversion rate was 2 to 4 times SO_2 rate.
NO_x	Removal rate	14 to 24% h^{-1}	Spicer (1979)	Boston urban plume, August.
NO_x	Removal rate	4% h^{-1}	Chang et.al (1979)	Annual average, Los Angeles.

5. Conclusions

A literature survey has been carried out into the seasonal variations of the wet and dry deposition rate, as well as the chemical transformation rate, of sulfur and nitrogen oxides, with particular reference to deposition and transformation parameters of relevance to long-range transport mathematical models. Both relevant theoretical and experimental results have been considered, although a critical evaluation of the references has not been attempted.

As indicated in Chapters 2, 3 and 4, from a theoretical viewpoint the deposition and transformation rates of sulfur and nitrogen compounds could potentially have a substantial seasonal variation. However, it is difficult to draw conclusions about the magnitude of this variation with any degree of confidence from the current theories, with the possible exception of the wet and dry deposition of sulfur dioxide and the photochemical component of its chemical transformation rate. Therefore, the available field data were also considered, although these were often too scanty to be of much assistance.

An attempt is made in Table 8 to summarize the available information on the seasonal variation of transformation/deposition rates for the sulfur compounds. It is not intended to recommend the values shown in this Table for use by the long-range transport modeller - much more experimental and theoretical work is needed before this will be possible - but rather, to indicate whether seasonal changes in the parameter of interest are expected to be greater or less than an order of magnitude (at present, little more than this can be done). The following conclusions can be made on the basis of Table 8 and the discussions in Chapters 2 to 4:

(1) The scanty available data suggest that the washout rates of sulfates (and probably nitrates) should be comparable in summer and winter. The rainout rates could be strongly dependent on storm type, and hence the time of year, because of the different mechanisms whereby particles can be incorporated into precipitation (-some data suggest variations of an order-of-magnitude or more).

(2) Experimental results and theoretical considerations suggest a seasonal variation of the wet scavenging coefficient for sulfur dioxide which can be up to several orders of magnitude, depending on the latitude, being most pronounced in the northern parts of America which receive appreciable amounts of snow in the winter. Probably the same conclusions also apply to nitrogen dioxide. Nitric acid vapour, being highly reactive with all kinds of surfaces, is expected to show a smaller seasonal dependence of the scavenging coefficient.

(3) The situation is too confusing at present to draw any conclusions about the seasonal dependence of the dry deposition rate for sulfates (or nitrates). In the winter, deposition velocities would seem to be 0.2 cms^{-1} or less, but values reported for summertime conditions range over an order of magnitude, including negative numbers.

(4) The dry deposition velocity of sulfur dioxide is expected, from available experimental and theoretical results, to show only a modest seasonal variation - generally, less than a factor-of-two or so in any given area. The same is probably true of nitrogen dioxide and nitric acid vapour.

(5) The gas-phase homogeneous component of sulfuric and nitric acid formation rates is relatively well understood, and has a strong seasonal variability, especially at the northern latitudes. However, our knowledge of the heterogeneous component, including in-cloud processes, is too poor at present to allow any conclusions regarding the seasonal dependence of the overall chemical transformation rate of sulfur and nitrogen oxides.

(6) For many of the parameters under consideration, during the winter months, rates are strongly dependent on latitude - e.g., photochemical conversion rates of sulfur and nitrogen oxides above $45^{\circ}N$ become negligible, as do also wet deposition rates of gases such as sulfur dioxide (because precipitation is largely in the form of dry snow). This indicates that not only the seasonal, but also the spatial variability of deposition and transformation rates should be taken into account in long-range transport models. Although it may be too early to speculate, the following approach does not seem unreasonable: during the summer months, one might assume, as a first approximation, the same values for deposition/transformation parameters irregardless of location, for each species of interest. During the winter months, while rates at the southerly latitudes might stay roughly the same as those in the summer, the models would include a dependence of deposition/transformation on latitude, which could be quite pronounced for some of the parameters (such as wet deposition of sulfur dioxide).

(7) For the sulfur compounds, more experimental data are badly needed, both under summer and winter-time conditions, particularly on wet and dry deposition rates of particulates and chemical transformation rates in regional scale air masses (as opposed to chimney plumes). Very little is also known about in-cloud transformation and deposition processes. For the nitrogen compounds, data are required in almost every area of interest, and immediate support for laboratory and field investigations into deposition and transformation rates of the major species (NO, NO_2, HNO_3, nitrates and PAN) is strongly recommended.

Table 8: Summary of Deposition and Chemical Transformation Rates for Sulfur Compounds

Parameter	Representative Range (Observed) Summer Conditions	Winter Conditions	Suggested (Winter/Summer) Ratio	Comments
$\Lambda(s^{-1})$ Sulfates	$\sim 10^{-5}$	$\sim 10^{-5}$	~ 1	- washout: based on very few data.
			10^{-1}(?)	- rainout: order-of-magnitude seasonal variations could be possible, depending on storm types (e.g., Scott, 1981).
$\Lambda(s^{-1})SO_2$	$(3\text{-}8)\times 10^{-4}$	$(1\text{-}25)\times 10^{-7}$	$\sim 10^{-3}$	- rainout: based on data of Summers (1977); applies to areas where wintertime precipitation is largely in the form of dry snow.
			~ 10(?)	- theoretically predicted possibility for areas which largely receive cold rain or wet snow during the winter.
$v(cms^{-1})$ Sulfates	(?)	< 0.2	(?)	- very large uncertainty about deposition velocity for sulfates.
$v(cms^{-1})$ SO_2	0.4-0.8	0.1-0.4	$\sim \frac{1}{2}$	- seasonal changes expected to be modest (i.e., not order-of-magnitude).
$SO_2 \rightarrow SO_4$ transformation rate h^{-1})	1-4 (chimney plumes) 1-30 (urban plumes)	< 1 (chimney plumes) 1-25 (urban plumes)	(?)	-gas-phase homogeneous processes should be small at latitudes greater than $45^{\circ}N$ in the winter. However there is too much uncertainty about the magnitude of heterogeneous processes, including in-cloud SO_2 conversion, to allow conclusions about seasonal variations.

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